

REMARKS

This amendment is respectfully submitted to place subject Application in condition for allowance. Claim 23 has been amended as suggested by Examiner to more distinctly claim the subject matter  
5 of the invention.

In view of the amendments submitted herein and previous filed papers, it is the position of Applicants that the instant Application is in condition for allowance.

Attention of Examiner is invited to previously presented Claim  
10 15 that was amended to recite the step of contacting all or at least a portion of the recovered organic phase with at least one immiscible liquid comprising a solvent having a dielectric constant suitable to selectively extract oxidized sulfur-containing and/or nitrogen-containing organic compounds. More particularly, original Claim 16  
15 recites the process according to claim 15 wherein the solvent has a dielectric constant in a range from about 24 to about 80. Applicants urge that Claims 12 and 14 to 25 inclusive, all claims now presented, are in condition for allowance.

Claim Rejections - 35 U.S.C. § 103

20 In the outstanding Office Action, Claims 12 and 14 to 25 were rejected under 35 U.S.C. § 103(a), as being unpatentable over U.S. Patent No. 1,972,102 in the name of William M. Malisoff (Malisoff), in view of U.S. Patent No. 6,217,748 in the name of Shigeto Hatanaka, Osamu Sadakane, and Hideshi Iki and assigned to Nippon  
25 Mitsubishi Oil Corp. (JP), (Hatanaka et al.), U.S. Patent No. 6,274,785 in the name of Walter Gore (Gore), and either GB 2262942A, or U.S. Patent No. 3,163,593 in the name of Alfred Bentley Webster, Norman James Herbert, and Richard Rigby (Webster et al.). Applicants respectfully traverse these rejections.

It is the position of Applicants that the Malisoff reference of record teaches a treatment for removal of sulfur from hydrocarbon oil by treating a hydrocarbon oil with a miscible treating solution containing a concentrated water solution of hydrogen peroxide and  
5 sufficient quantity of acetic acid to render the treating solution miscible with the oil, and thereafter adding an equivalent volume of water to obtain a resulting dilute aqueous phase which separates from the treated oil phase (Malisoff, for example, at page 1, lines 49 to 59, and page 2, lines 3 to 5). In example 1 of Malisoff, the  
10 resulting dilute aqueous phase containing more than 60 percent water (calculated without including any water formed by reaction of hydrogen peroxide).

By contrast, instant claims include a key step of contacting a high-boiling, sulfur-rich, mono-aromatic-lean, petroleum distillate  
15 fraction with an immiscible phase comprising at least one organic peracid or precursors of organic peracid in a liquid phase reaction mixture. Maintaining the reaction mixture substantially free of catalytic active metals and/or active metal-containing compounds and under conditions suitable for oxidation of one or more of the  
20 sulfur-containing and/or nitrogen-containing organic compounds including temperatures in a range upward from about 50° C. to about 150° C. are recited elements of the invention. Blending components containing less sulfur and/or less nitrogen than the oxidation feedstock are recovered from the reaction mixture.  
25 Advantageously, at least a portion of the immiscible peracid-containing phase is also recovered from the reaction mixture and recycled to the oxidation. Integrated processes of this invention may also provide their own source of high-boiling oxidation feedstock derived from other refinery units, for example, by  
30 hydrotreating a petroleum distillate. It is the position of Applicants that their novel processes differ in kind, not merely in degree, from the process described in the Malisoff reference of record.

Applicants agree with Primary Examiner Griffin that critical elements of their novel process, as recited by the instant claims, are not disclosed or suggested in the Malisoff reference of record.

5 However, without extensive and impermissible use of hindsight one skilled in the art at the time the novel invention was made should not have found in the references of record relied upon by Examiner disclosure or suggestion of the process according to the instant claims.

10 Oils treated according to examples in the Malisoff reference of record initially contained sulfur at levels of 0.21, 1.12, and 0.25 percent sulfur. However the products of the Malisoff treatments, resulted in products containing sulfur levels of 0.16, 0.88 and 0.10 percent sulfur (1,600 ppmw, 8,800 ppmw and 1,000 ppmw). These levels of sulfur are very high in view of sulfur specifications for  
15 transportation fuels. Legislation on sulfur in diesel fuel in Europe, Japan and the U.S. has recently lowered the specification to 0.05 percent by weight maximum sulfur in Diesel fuel, and indications are that future specifications may go far below the current 0.05 percent by weight level.

20 By contrast, all products of an alumina treatment according to Applicants' Example 14 had a sulfur concentration of less than 3 ppmw, and in general 1 ppmw sulfur.

By the contacting step that instant claim recite, the selected petroleum distillate fraction with a peracid-containing immiscible  
25 phase in a liquid reaction mixture maintained substantially free of catalytic active metals and/or active metal-containing compounds, the tightly substituted sulfides are oxidized into their corresponding sulfoxides and sulfones with negligible if any co-oxidation of mononuclear aromatics. These oxidation products due to their high  
30 polarity, can be readily removed by separation techniques such as sorption, extraction and/or distillation. The high selectivity of the

oxidants, coupled with the small amount of tightly substituted sulfides in hydrotreated streams, makes the instant invention a particularly effective deep desulfurization means with minimum yield loss. The yield loss corresponds to the amount of tightly substituted sulfides oxidized. Since the amount of tightly substituted sulfides present in a hydrotreated crude is rather small, the yield loss is correspondingly small.

It is the position of Applicants that the Malisoff reference of record does not suggest the essence of their novel multi-step process as recited according to instant Claims 12 and 14 to 25 inclusive.

The Hatanaka et al. reference of record describes a four-step hydrodesulfurization (HDS) of a sulfur-containing petroleum hydrocarbon diesel gas oil. The gas oil is catalytically hydrodesulfurized at 300° C. to about 500 ppm sulfur in a first HDS step. Step two is distillation at a cut point temperature in a range of 320 to 340° C. Step three is a second HDS of only the heavy fraction of the distillation at up to 380° C. The twice hydrodesulfurized heavy fraction (90 ppm sulfur) is mixed with the light fraction of the distillation (10 ppm sulfur) to a sulfur content of up to 0.01%. For example, a product having 50 ppm sulfur is reported by Hatanaka et al. as Example 3. As noted above, all products of an alumina treatment according to Applicants' Example 14 had a sulfur concentration of less than 3 ppmw, and in general 1 ppmw sulfur.

Obvious disadvantages of the Hatanaka et al. process include the costs of the additional hydrogen and energy required for both the distillation and further hydrodesulfurization steps. While Hatanaka et al. state the hydrogen sulfides from the two HDS steps may be removed from the off-gas by an amine absorption arrangement, carbon oxides are also by-products of the HDS steps. Generation of the additional hydrogen also produces more carbon

dioxide. These are especially critical at a time when most industries are striving to limit the amount of emitted "green house" gas such as carbon dioxide.

5 Less obvious disadvantages of the second HDS in the Hatanaka et al. process include a loss of non-sulfur multi-ring aromatic hydrocarbons to saturated non-aromatic ring compounds. This has negative fuel property/quality consequences such as affecting the pour point, reducing the lubricity, and reducing the fuel value (Btu/volume) of diesel fuel. A diesel fuel rich in aromatics have a  
10 higher Btu/volume and give more miles per gallon.

The oxidation step in Applicants' novel process is very specific in the targeting of sulfur hetroaromatic compounds. Oxidation of these offending sulfur hetroaromatics is selective and other aromatic hydrocarbons not containing sulfur or nitrogen are  
15 unaffected by the process.

Danping Wei and H. A. Spikes reported results of their investigation of the main chemical factors influencing the lubricity of diesel fuels, diesel fuel fractions and model fuels in a paper titled THE LUBRICITY OF DIESEL FUELS (Wear, 111 (1986) 217 - 235).  
20 Under test conditions the used, sulfur-containing components were found to be pro-wear. Polyaromatic species and, in particular, oxygen-containing components, were found to reduce wear significantly.

Contrary to the position of Examiner, substituting the  
25 oxidation treatment of Malisoff for the second HDS of Hatanaka et al. does not produce an equivalent result, because as shown above, the oxidation treatment of Malisoff is different in kind from instant claims which include a key step of contacting a high-boiling, sulfur-rich, mono-aromatic-lean, petroleum distillate fraction with an  
30 immiscible phase comprising at least one organic peracid or precursors of organic peracid in a liquid phase reaction mixture.

By contrast Applicants' novel process includes a catalyzed, hydrogen peroxide, promoted oxidative desulfurization of a sulfur-rich, mono-aromatic-lean fraction without further production of carbon dioxide or hydrogen sulfides. An additional advantage of Applicants' novel oxidative desulfurization process is that oxidation is selective to sulfur and nitrogen containing heteroaromatic compounds, i.e. does not saturate the non-sulfur, non-nitrogen multi-ring aromatic hydrocarbons.

Examiner used the Gore reference of record to disclose treating and recycling the oxidant. However, practice of recycle according to the disclosure of Gore on hydrogen peroxide and acetic acid results in a critical accumulation of a high water concentration. Each mole of hydrogen peroxide used results in formation of mole of water. As water concentration increases, the equilibrium concentration of peracetic acid is reduced, which must decrease the efficiency of the oxidation.

By contrast, Claim 23 recites Applicants' novel process according to claim 21 further comprising treating at least a portion of the separated peracid-containing phase to remove and at least a portion of the sulfur-containing and nitrogen-containing organic compounds and water contained therein, and thereafter recycling to the reaction mixture at least a portion of the treated peracid-containing phase having a water content of less than 60 percent by volume.

Examiner used the GB reference of record to disclose treatment of a treated oil with an alumina adsorbent. However, according to the GB reference an oxidized hydrocarbon material is washed with 2 Normal sodium sulfite and thereafter washed with water to remove residual sodium sulfite, prior to treating the twice washed hydrocarbon material with the alumina adsorbent.

Examiner used the Webster et al. reference of record to disclose treatment of an oil obtained from an oxidizing process with

an alkaline material as suggested by Webster because a material with a reduced amount of sulfur will be obtained.

Contrary to the position of Examiner, Webster et al. report their thermal treatment in the presence of lime of an oil obtained from an oxidizing process, resulted in a material having a higher level of sulfur than treatment without lime, 2.52 percent sulfur with lime, 2.03 percent sulfur without lime (Webster et al. column 4, lines 25 to 45).

It is the position of Applicants that instant Claims 12 and 14 to 25 inclusive, meet all requirements under 35 U.S.C. § 103(a).

Affidavit under Rule 1.132

An affidavit under Rule 1.132 of Dr. WILLIAM H. GONG on the 18th day of December, 2003, identified as Paper No. 11, is hereby presented to further the prosecution of subject Application. In particular, the affidavit of Dr. Gong supports instant Claims 12 and 14 to 25 inclusive which have been drafted and amended to claim Applicants' novel invention as described in the specification and original claims of subject application

In 1984 William H. Gong received a Bachelor of Science degree in Chemistry from the Illinois State University, Normal, Illinois, and a Doctor of Philosophy Organic Chemistry in 1990 from the Iowa State University of Science and Technology, Ames, Iowa.

From 1990 to the present, Dr. Gong has been employed by Amoco Chemical Company, now BP Chemicals, a corporation of the State of Delaware, and have the position of Research Associate Scientist. His responsibilities have included "step-out" research in homogeneous catalytic oxygenation of alkylaromatic hydrocarbons, and reaction mechanism, and development of processes to catalytically oxygenate distillates and to selectively desulfurize distillates. Among his present professional assignments are

Technical Manager of Innovation Portfolio Group responsible for development of new catalytic oxidations processes; Technical consultant in areas of catalytic oxidation chemistry and reaction mechanism; and Manager of University Collaborations for the  
5 technology department of business unit.

Applicants and their undersigned Attorney appreciate Examiner's attention to the arguments of Dr. Gong in further consideration of this matter.

Base on the amendments submitted, herein and previously,  
10 and Paper No. 11, an affidavit under 37 CFR. § 1.132, Applicants urge that Claims 12 and 14 to 25 inclusive, all claims now presented, are in condition for allowance. Applicants respectfully request Primary Examiner Griffin to pass subject application for allowance.

15 Do not hesitate to contact Frederick S. Jerome whose telephone number is (630) 832-7974 (FAX (630) 832-7976) if additional assistance is needed regarding this paper or earlier papers for Applicants.

Respectfully submitted,

20



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25

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09/779,285 filed 2/8/01

EXHIBIT A WILLIAM H. GONG AFFIDAVIT UNDER RULE 1.132



Customer No. 04249

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of: ) Paper No. 11  
)  
APPLICANTS: WILLIAM H. GONG, )  
MONICA R. REGALBUTO & )  
GEORGE A. HUFF JR. )  
)  
)  
SERIAL NO: 09/779,285 ) Group Art Unit:  
) 1764  
)  
FILED: February 8, 2001 ) Examiner:  
) Walter D. Griffin  
)  
)  
FOR: PREPARATION OF COMPONENTS FOR ) Attorney Docket  
REFINERY BLENDING OF ) No.: 37,248  
TRANSPORTATION FUELS )

Commissioner for Patents  
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Alexandria VA 22313-1450

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**AFFIDAVIT UNDER 37 CFR § 1.132**

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<u>CERTIFICATE OF MAILING</u>	
I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to:	
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on <u>December 23</u> , 2003	By <u>Carol M. Neth</u>
(Date)	(Signature)
<u>CAROL M. NETH</u>	
(Typed or Printed Name of Person Signing Certificate)	

**AFFIDAVIT UNDER 37 CFR § 1.132**  
**of Dr. WILLIAM H. GONG.**

5           1.     I, WILLIAM H. GONG being duly sworn, depose and say:

          2.     That I reside at 900 Fairfield Avenue, Elmhurst, Illinois  
60126.

          3.     In 1984 I received a Bachelor of Science degree in  
Chemistry from the Illinois State University, Normal, Illinois, USA.  
10   My undergraduate research was directed to methods for upgrade  
of Illinois No. 6 coal.

          4.     I received a Doctor of Philosophy Organic Chemistry in  
1990 from the Iowa State University of Science and Technology,  
Ames, Iowa, USA. My dissertation research was development of  
15   palladium-based homogeneous catalytic methods and organic  
synthesis.

          5.     From 1990 to the present, I have been employed by  
Amoco Chemical Company, now BP Chemicals, a corporation of the  
State of Delaware, and have the position of Research Associate  
20   Scientist. My responsibilities have included "step-out" research in  
homogeneous catalytic oxygenation of alkylaromatic hydrocarbons,  
and reaction mechanism, and development of processes to  
catalytically oxygenate distillates and to selectively desulfurize  
distillates. Among my present professional assignments are  
25   Technical Manager of Innovation Portfolio Group responsible for  
development of new catalytic oxidations processes; Technical  
consultant in areas of catalytic oxidation chemistry and reaction  
mechanism; and Manager of University Collaborations for the  
technology department of business unit.

6. I am one inventor of the claimed subject matter of the above identified patent application.

7. I have read Primary Examiner Griffin's Office Action, mailed October 28, 2003, for our application and the references  
5 relied upon to reject of our claims.

8. U.S. Patent No 1,971,102 in the name of Malisoff teaches treatment of feeds without any attention to the possibility that there are something in the feed that will also consume the oxidant. Malisoff used feeds that are broadly classified as  
10 "hydrocarbon oils". For instance, Example-1 used "cracked petroleum distillate", Example-2 used gas-oil (a distillate of a certain boiling point), and Example-3 used naphtha (which can be anything)). None of the feeds were specifically hydrotreated prior to oxidation, an important consideration.

15 9. Our claims recite "hydrotreating a petroleum distillate consisting essentially of material boiling between about 50° C. and about 425° C." and "fractionating the hydrotreated petroleum distillate by distillation to provide ... a high-boiling feedstock consisting of a sulfur-rich, mono-aromatic-lean fraction" for our  
20 oxidation treatment step. We apply our oxidation treatment step only to a hydrotreated feed for two reasons. 1) to remove olefins and 2) to remove easily hydrotreated sulfur impurities.

10. If the feed is not a distillate, it could also contain transition metals that can also rapidly decompose the peroxide  
25 (again, Malisoff did not specify). Such metals (i.e. iron) could catalyze the Fenton reaction.

11. If hydrotreating did not occur prior to oxidation, much of the oxidant would have been wasted on the oxidation of the olefins to produce epoxides, something not useful for the particular  
30 product. This was not anticipated in U.S. Patent No 6,217,748 in the name of Hatanaka et al. (i.e. they claimed that hydrotreating of

the feed is only intended to reduce some of the sulfur prior to distillation and desulfurization of the high boiling stream).

12. Furthermore, Malisoff teaches using solutions too high in water, which would be an impediment to the oxidation.

5        13. By contrast we claim using a "peracid-containing phase having a water content of less than 60 percent by volume". Thus, during our oxidation reaction, we obtain an unexpected benefit by adjusting the water concentration in the oxidation solution. As we decreased the amount of water in the immiscible oxidation  
10 solution, we discovered that the concentration of oxidized sulfur impurities partitioned into the oxidation solution (water, hydrogen peroxide, and acetic acid) increased. Therefore, by merely decanting the oxidation solution from biphasic mixture, we can remove over 60% of the oxidized sulfur impurities without doing  
15 anything else.

14. U.S. Patent No 6,274,785 in the name of Gore teaches treatment which requires a second step that is devoted to wholly extracting all of the oxidized sulfur compounds. We don't depend on the second step to extract all of the sulfur compounds.

20        15. At the water level taught by Malisoff, it is our experience that almost no extraction of the oxidized sulfur compounds are found in the oxidation solution. Additionally, the oxidation is drastically reduced in efficiency in the presence of this much water.

25        16. The Hatanaka et al. process teaches an initially hydrotreating of feed followed by separation of low and high boiling fractions. The intent of the hydrotreating is to remove some of the sulfur. The low boiling distillation fraction contains almost no sulfur while the high boiling fraction contains a high  
30 level of sulfur impurities. Hatanaka et al. then hydrotreats the high boiling fraction at more severe conditions to reduce the sulfur

concentration of this fraction. The product is then blended with the light fraction to produce an overall, lower sulfur product.

17. It is generally known to those ordinarily skilled in the art, the hydrodesulfurization (HDS) of high boiling, heteroaromatic sulfur impurities require more severe conditions, which result in compositional changes that are not obtained in the oxidative desulfurization process (ODS).

18. For example, it was recently published in *Chemical & Engineering News* (October 27, 2003, pp. 40 - 41), when severe HDS conditions are applied to drive the sulfur concentration down to 30 to 15 ppmw, light hydrocarbons are unavoidably produced due to unwanted hydrocracking of the product. This hydrocracking consumes expensive hydrogen beyond the amount expected for the HDS process. Therefore, hydrocracking also has the unwanted consequence of lowering the yield of the liquid fuel.

19. Additionally, recently at the *Europa Cat VI* technology conference (August 31 - September 4, Innsbruck, Austria), a number of papers were presented which specifically described the significant challenges to producing an ultra-low sulfur diesel product.. The following outlines these challenges.

20. Catalytic, deep hydrodesulfurization is interfered by the presence of hydrocarbons such as naphthalenes and other mono-aromatics. These impurities occupy the active sites of the HDS catalyst. These aromatics are chief components in a distillate feed.

21. Organonitrogen compounds bind very effectively to these catalyst sites to prevent desulfurization of the sulfur impurities, especially the varieties that prevent the process from achieving the 15 to 30 ppmw levels. As the desulfurization occurs, the concentration of sulfur impurities is reduced to a point where it matches the concentration of the nitrogen impurities. At this

point, nitrogen will prevent the sulfur impurities from being converted

22. Even the product of HDS, hydrogen sulfide ( $H_2S$ ), was shown to be a strong HDS inhibitor because of its ability to poison the HDS catalyst. This also effectively prevents the process from reaching the intended ultra-low sulfur targets.

23. None of the above are challenges for our process. Our novel process is not interfered by aromatic hydrocarbons. Our process takes out the aromatic amines, without cracking. These all constitute superior advantages to the HDS of the high boiling stream that Hatanaka et al. teach.

24. Based on the above information, I respectfully argue with the Examiner that those who are ordinarily skilled in the art would not say that both the Hatanaka et al. HDS process and our novel process produce the same results because the results are in fact very different. The HDS process encounters severe challenges to achieve the ultra-low sulfur levels, which the our novel process does not encounter because the nature of the chemistry is vastly different.

25. In response to our arguments with respect to U.S. Patent No 6,274,785 in the name of Gore, Examiner wrote, "Gore teaches that used oxidant is pumped into an oxidant recycler where it is treated and oxidized back up to reactive form and recycled". With all due respect, this is not fair and it reflects a huge benefit of doubt given to Gore. For example, what is the definition of "treated"? I doubt very much that the Examiner appreciated the details of the oxidation.

26. The Examiner likely referred to Fig 1 (Sheet 1 of 6) where it shows a box labeled "Oxydant Recycler". The "Oxydant Recycler" is fed by a source of "O3 or  $H_2O_2$  Feed". Within this context, this would suggest that the Oxydant Recycler is a blending

vessel as it combines the returning spent "oxidant" with a source of the oxidant.

27. The Examiner wrote "this indicates that the recycled oxidant is treated so that it is essentially the same as the original oxidant." I respectfully submit, what the Examiner failed to recognize is that the active oxidant is not the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) because the hydrogen peroxide is not activated towards oxidation of the sulfur impurity without it first transformed to the active oxidant.

28. The purpose of the acetic acid is for it to react with the hydrogen peroxide to form, *in situ*, the active oxidant, peroxyacetic acid. The combination of water, acetic acid, hydrogen peroxide, and peroxyacetic acid exists in an equilibrium that can be greatly influenced by adjusting the concentrations of any of these four components.

29. I respectfully contend that Gore never taught that the water concentration must be reduced in the recycle stream. Therefore, I argue that by merely replenishing the hydrogen peroxide to maintain a certain constant concentration of hydrogen peroxide would result in an increasingly less efficient oxidation *per* recycle pass of the oxidant. This is because the water concentration would continue to build up and drive the equilibrium towards the oxidatively inactive hydrogen peroxide and acetic acid. What must be noted is that water is also added when hydrogen peroxide is added, so water removal must also account for the water from the oxidant. Therefore, to be able to say that a constant concentration of hydrogen peroxide oxidant in the stream implies that the oxidant stream is now fully capable of constant conversion is entirely false.

30. Again, if dehydration is not practiced, then one has a lower equilibrium concentration of the peroxyacetic acid. This in net effect makes the oxidation less effective with every pass. This



decreasing level of effectiveness occurs even though one maintains a constant concentration of hydrogen peroxide in the "Oxidant Feed" stream. Nowhere in Gore's patent is there a mention of the need to practice dehydration, but we would argue that that it is  
5 crucial for one to practice recycle. Instead, only one sentence appeared in Gore's patent about recycle: "The oxidant can then be regenerated for re-use." (Col. 4, line 57).

31. I continue to respectfully maintain that in Webster et al. their use of lime ( $\text{CaCO}_3$ ) is for a vastly different purpose than  
10 our use of an alkaline agent. Specifically, Webster et al. use lime to aid in the decomposition of the oxidized sulfur impurities at very high temperature (see U.S. Patent No 3,163,593, Claim 2).

32. Their process is to oxidize the sulfur impurities in the feed to such things as sulfones. Then all of the solvent is removed  
15 via distillation. This would logically leave behind only the hydrocarbon which contains the oxidized sulfur compounds (sulfones). The following step is to thermalize the sulfone intended to crack off the sulfur oxide to leave behind the hydrocarbon. However, what actually happened in this process is that it  
20 produced a significant percentage of lights, which Webster et al. showed by the "percent distillate" in Example IV, Table I and Example V, Table II. Then lime is added in Example VI. They taught that the added lime assisted in the decomposition by reducing the "percent distillate" and increased the "percent  
25 residual oil" (see U.S. Patent No 3,163,593, Table III in Example VI).

33. By contrast, we use an alkaline substance (aqueous basic solution) in a manner that is completely different from that of Webster et al. We use it to neutralize residual traces of the  
30 acidic solvent (acetic acid) in the final oxidized diesel product.

34. Webster et al. never taught that the use of lime was intended to neutralize/remove traces of solvent. Instead, they

taught that after all of the solvent is distilled overhead and prior to the addition of lime to aid in the decomposition step. Again, Webster et al. taught that the addition of lime reduced coking in the thermal decomposition step, reduce the percent distillate  
5 (lights going overhead in the cracking), and increased the percent residual oil.

36. Examiner avers that "Both the oxidation and HDS steps result in the removal of sulfur. Therefore, the examiner maintains that one having ordinary skill in the art would expect similar  
10 results from either the HDS or oxidation steps". I respectfully submit that product of our novel process in fact is not "similar" to product from the HDS step.

37. Attention of Primary Examiner Griffin is invited to my EXHIBIT A which is a copy of an article ("The Lubricity of Diesel  
15 Fuels" Wei, D.; Spikes, H. A. *Wear*. 1986, 111, 217-235), that reports the findings of components that are anti-wear and pro-wear. Sulfur hetroaromatics promote wear, nitrogen hetroaromatics will prevent wear if present in high concentration, but aromatics, particularly polyaromatic hydrocarbons will prevent  
20 wear. Respectfully, I submit that products of our novel process in fact are not "similar" to products from the HDS step.

38. The HDS process in fact produces a product with poor lubricity. It was thought at first that the sulfur impurities help to prevent wear, but that is not true. According the published  
25 research, it is the polyaromatic hydrocarbons that reduce wear. HDS effectively removes a substantial amount of polyaromatic hydrocarbons through hydrogenation. The unexpected advantage of our novel process is that it preserves these beneficial polyaromatic hydrocarbons.

39. Therefore, I must content that both processes produce substantially different result in terms of fuel properties, which are highly important. Our novel process clearly produced a product  
30

09/779,285 filed 2/8/01

that has unexpectedly better properties than the HDS process  
because our process preserves the aromatics for lubricity.

AND FURTHER AFFIANT SAYETH NOT.

5 William H. Gong  
WILLIAM H. GONG

STATE OF ILLINOIS     )  
                                  ) SS.  
COUNTY OF DUPAGE    )

Sworn to and subscribed before me, a Notary Public, by said  
10 WILLIAM H. GONG, on this 18 day of December 2002. 3 KGS



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## THE LUBRICITY OF DIESEL FUELS

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(Received October 14, 1985; accepted January 29, 1986)

### Summary

The main chemical factors influencing the lubricity of diesel fuels have been investigated by carrying out wear tests on diesel fuels, diesel fuel fractions and model fuels.

It has been found that, under the test conditions used, sulphur-containing components were pro-wear. Nitrogen-containing components tended to reduce wear but only at concentrations in excess of those normally found in diesel fuels. Polyaromatic species and, in particular, oxygen-containing components, were found to reduce wear significantly at concentrations normally found in fuels.

### 1. Introduction

Liquid hydrocarbon fuels, such as gasoline, jet fuel and diesel, need to possess a modicum of lubricating ability to protect sliding surfaces in fuel pumps, injection valves and other moving parts. This requirement was first recognized in the mid-1960s, when improvements in refining and treatment processes led to the production of some very pure aviation fuels. Their consequent poor lubricity resulted in a spate of seizure and wear problems [1, 2].

In response to these performance difficulties a good deal of research effort was expended, both in measuring the lubricity of aviation fuel and in attempting to identify the active lubricating components in fuel. Neither of these areas of interest has been fully resolved, however. There exists no recognized test for fuel lubricity and many of the standard wear and friction tests are too severe to differentiate between fuels. A wide range of fuel components have been reported as contributing to good lubricity, but these reports are generally contradictory and limited in scope.

Most of the work so far has been carried out on aviation fuels, some of which are very highly refined and operating at the limits of their lubricity.

Recently, however, the converging trends of increasingly rigorous fuel treatment and of higher fuel injection pressures have focused attention on the less severely refined automotive diesel fuels. In this paper an investigation into the wear-preventing characteristics of such diesel fuels is described. The main aims were (a) to develop a test method to distinguish between the small differences in the lubricities of the various diesel fuels, (b) to analyse and separate the various polar fractions of diesel fuels and to determine their lubricities and (c) to estimate the relative effectiveness of natural trace components in contributing to diesel fuel lubricity.

In this paper the term "lubricity" is used according to the very broad definition suggested by Appeldoorn and Duijck [3]: "If two liquids have the same viscosity, and one gives lower friction, wear, or scuffing, then it is said to have better lubricity."

## 2. Background

Automotive diesel fuel, like other petroleum products, are complex and variable mixtures whose compositions depend on the source of the crude petroleum, the separation method and the purification techniques used. There are, broadly, two components of diesel fuel in use: straight-run distillate and upgraded residues. The former is a definite boiling fraction collected in the main petroleum distillation process. The latter is produced by cracking higher boiling residues and therefore tends initially to contain more non-hydrocarbon and aromatic impurities and to form more complex mixtures. It is common for straight-run distillate and upgraded residues to be blended to obtain finished diesel fuel.

As well as the initial distillation and cracking processes the preparation of a diesel fuel also involves one or more treatment processes, such as solvent extraction, caustic treatment and hydrotreating, to remove undesirable impurities. Over the past few years a range of hydrogenation treatments of varying severity have become common. These are especially effective at removing polar and unsaturated components and, on the basis of jet fuel experience, are potentially responsible for a large decrease in fuel lubricity.

A notional but representative diesel fuel composition is summarized in Table 1. Sulphur impurities are typically mercaptans, sulphides and thiophenes [4]. Nitrogen impurities are usually basic pyridines and quinolines and non-basic pyrroles, carbazoles and indoles [5]. Some naphthenic acids, phenols and other oxygen-containing impurities are present in diesel fuel, but there have been few systematic attempts to measure their concentrations [6].

With a wide variability in composition, even from batch to batch, it becomes important to understand how the various components in diesel fuel, listed in Table 1, contribute to lubricity. However, there is remarkably little agreement in the literature about this. High molecular weight components [7], naphthalenes [8], polyaromatics [8, 9], sulphur compounds [8, 10],

TABLE 1  
Representative diesel fuel composition

Component	Typical amount (wt. %)
Paraffins	39
Naphthenes (cyclopentanes)	35
Monoaromatics	10
Diaromatics	13
Polycyclic aromatics	3
S	0.5
N	0.03 (200 ppm)
O	0.01 (rarely reported)

nitrogen compounds [11], polar compounds excluding sulphur and nitrogen-containing compounds [3] and oxygen compounds [9] have all been claimed to be responsible for good lubricity in fuel.

One cause for this variation appears to be the wide variety of test methods and thus loads, speeds, metallurgies and temperatures employed when determining the lubricity of fuel. The marginal lubricating capabilities of fuels compared with lubricants means that most conventional lubricant tests are at the limit of their sensitivities when used with fuel, with failure often occurring at the lowest load possible. Conventional scuffing and wear testers have been employed but have often been found to have test conditions too severe to differentiate between the poor lubricities of different fuels [12, 13].

In the mild conditions relevant to fuel performance, loads tend to be quite low and this can result in the operation of some tests in mixed boundary-hydrodynamic or boundary-elastohydrodynamic conditions. Since considerable variations in viscosity are found between diesel fuels (the 4D grade, for example, spans 5.5 to 24.0 cS [14]), this means that such tests will reflect fuel viscosity effects rather than intrinsic lubricity. A low load dwell test rig has been used to measure the life of fuel films [15] but is very sensitive to the volatility of the fuel and is also strongly affected by trace high molecular weight materials [7].

## 3. Wear test method

In this study a high frequency reciprocating machine was employed. Details of this have been given elsewhere [16] and a schematic diagram of the rig is shown in Fig. 1. Its combination of low load, low speed and point contact geometry ensure low frictional heating and negligible hydrodynamic lift, especially at the ends of the contact stroke where the velocity of the upper specimen reverses. A particularly useful feature of the test machine in this investigation was its ability to use very small fuel samples, which permitted studies on separated fuel fractions.

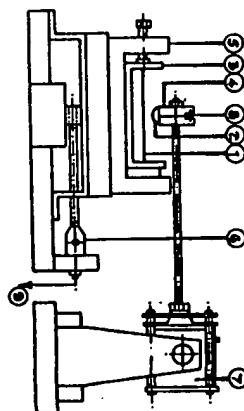


Fig. 1. Schematic diagram of the high frequency reciprocating test rig: 1, test plate; 2, test ball; 3, oil bath; 4, chuck; 5, heating block; 6, piezoelectric crystal force gauge; 7, vibrator; 8, loading pin.

The contact consisted of a loaded upper ball 6.35 mm in diameter which oscillated against a static lower flat. The contact was fully immersed in fuel. The friction and electrical contact resistance are monitored throughout a test and wear is measured from the scar diameter on the ball at the end of a run.

In this study the load used was 2.2 N, the stroke length 0.5 mm and the frequency of oscillation 50 Hz. All tests were conducted at room temperature ( $18 \pm 2^\circ\text{C}$ ) and the test specimens were both En81 steel. The Vickers hardness of the balls was 845 HV but the flats were not heat treated and had a Vickers hardness of 190 HV. A new ball was used for each test and the lower plate was cleaned and polished to  $1.0 \pm 0.1 \mu\text{m}$  centre-line average prior to each run. Specimens, holders and lubricant bath were all cleaned ultrasonically in a succession of Analar toluene, ethanol and acetone prior to testing.

The tests reported in this paper all lasted 75 min. The wear scar could be measured to  $\pm 0.002$  mm and preliminary studies showed good repeatability for friction, contact resistance and wear, with scar diameters within  $\pm 2\%$  for the same fuel.

An assumption made in this study was that the lubricity of fuels in diesel pumps correlates with wear scar measurements in the high frequency reciprocating machine, although it should be appreciated that the validity of this assumption is ensured only for machine elements of similar geometries and metallurgy, operating under similar loads and kinematic conditions.

#### 4. Wear performance of diesel fuels

14 commercial diesel fuels were tested. Some details of the fuels, together with their wear performance, are listed in Table 2. A few preliminary observations can be made.

(a) Considerable differences in wear performance between fuels are produced by the test method.

TABLE 2  
Properties and wear performance of diesel fuels

Fuel	Wear scar diameter (mm)	Viscosity (cSt) at $40^\circ\text{C}$	Cloud point ( $^\circ\text{C}$ )	Pour point ( $^\circ\text{C}$ )	Final boiling point ( $^\circ\text{C}$ )	Aromatics (vol.%)	S (wt.%)	N (ppm)	Dyed	Further comments
1	0.32	2.58	-10	-	344	30.0	0.19	65	Yes	
2	0.23	4.38	2	0	381	44.3	0.22	170	No	
3	0.23	3.24	-10	-	355	35.8	0.37	160	No	
4	0.19	4.38	5	0	387	44.9	0.33	210	No	
5	0.27	2.50	-11	-	346	53.7	0.37	200	Yes	
6	0.22	3.72	-9	-15	355	26.2	0.26	130	No	
7	0.175	3.80	8	-1	387	55.9	0.36	250	Yes	
8	0.24	2.59	-19	-30	352	-	0.15	130	No	
9	0.28	2.59	-11	-	346	53.7	0.37	270	Yes	Fuel 5 + cetane improver
10	0.19	3.80	3	-1	387	55.7	0.36	320	No	Fuel 7 + cetane improver
11	0.21	4.14	-	-	427	27	0.29	-	No	
12	0.17	3.40	-	-	491	30	0.37	85	Yes	Straight run
13	0.35	-	-	-	-	-	-	115	No	Hydrotreated
14	0.46	-	-	-	-	0	0	-	-	Hexadecane

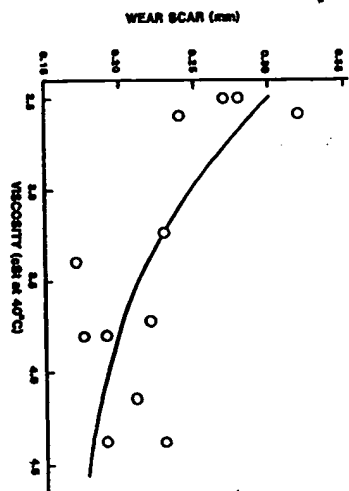


Fig. 2. Variation in wear with viscosity for a range of diesel fuel.

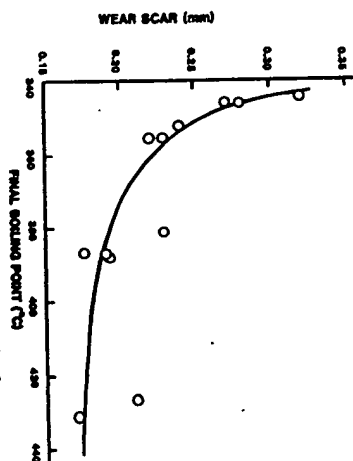


Fig. 3. Variation in wear with final boiling point for a range of diesel fuel.

- (b) When oil 12, a typical straight-run fuel, was percolated through an alumina column, wear increased by 2.5 times.  
 (c) A known hydrocracked fuel (fuel 13) showed far greater wear than a straight-run fuel (fuel 12).  
 (d) A pure saturated hydrocarbon, hexadecane, passed through an alumina column gave the poorest performance of all.  
 (e) There was a general correlation between the contact resistance and the antiwear performance, i.e. the greater the contact resistance build-up the lower was the wear.

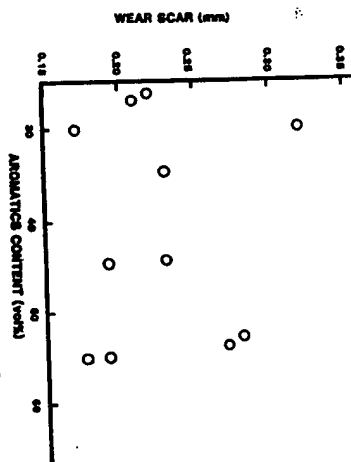


Fig. 4. Variation in wear with aromatic content for a range of diesel fuel.

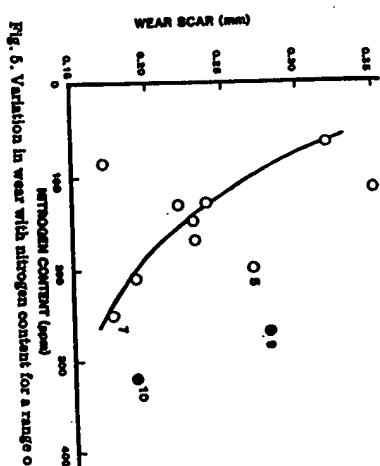


Fig. 5. Variation in wear with nitrogen content for a range of diesel fuel.

One very simple approach to assessing how the lubricity of diesel fuels arises is to see how the wear scar varies with the physical and chemical properties of the fuel. Figures 2-6 show the wear scar character plotted against viscosity, final boiling point, aromatic content, nitrogen content and against sulphur content for the range of fuels tested. There appears to be a broad correlation between a decrease in the wear scar and increased viscosity, fuel boiling point, nitrogen content and sulphur content although the curves drawn in Figs. 2, 3 and 5 are very approximate and should be regarded as drawn of trends only. For the nitrogen content curve it should be noted that fuels 9 and 10 have their nitrogen artificially increased by the inclusion

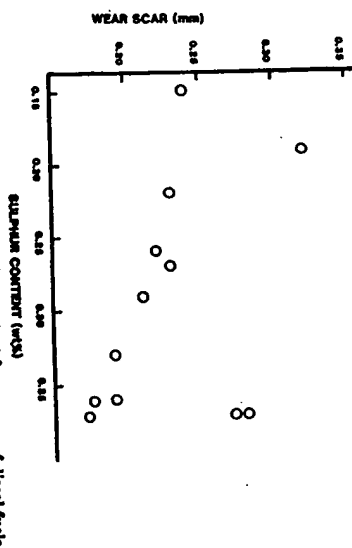


Fig. 6. Variation in wear with sulphur content for a range of diesel fuels.

of a nitrile antiknock additive. Clearly this additive does not contribute to lubricity.

Unfortunately this simple parametric approach is not very useful because characteristics such as viscosity, nitrogen content etc. tend to be associated in diesel fuels. A fuel with a high boiling point tends also to have a high concentration of polar impurities and a high viscosity so that the effects of the separate factors cannot be readily distinguished. It will be indicated later in this paper that the apparent reduction in wear with increasing sulphur content is probably spurious and results from associated increases in nitrogen and polar content.

Two methods were employed in this study to overcome the problem. Fuels were separated into fractions for testing and also model compounds were used to simulate trace impurities.

## 5. Separation of diesel fuel

### 5.1. Separation methods

The fact that percolation of diesel fuel through an alumina column resulted in increased wear suggests that active lubricity components are removed by this process. Chromatographic methods were therefore employed to separate diesel fuel into fractions of different polarities.

A number of techniques have been used in the past to separate heavy oil distillates [17, 18] but many of these involve polar and non-volatile solvents such as water and pyridine that are subsequently difficult to remove from separated fractions and also tribochemically active. The principal method adopted in this study was a combination of displacement and percolation chromatography through an alumina column. Approximately

100 cm<sup>3</sup> of fuel were poured into the top of an alumina column 80 cm high and of radius 15 mm. Four fractions were collected from fuel percolating and of radius 15 mm. Four fractions were collected from fuel percolating directly through the column. Then ethanol was poured slowly onto the column to elute the remaining fuel. A head of 10 cm of ethanol was maintained in the column until the alumina became completely white. This usually took about 1 day and up to six further eluted fractions were collected. This technique provided a rapid separation of quite large samples of fuel and sufficient of each fraction for separate wear testing.

A second chromatographic technique was also explored with a view to separating the most polar materials in diesel fuel. This involved a two-stage process. In a preliminary separation, adsorption chromatography was used, with a kiesel gel column. The fuel was fully adsorbed in the column and then eluted with a sequence of increasingly polar solvents and solvent mixtures from benzene through to methanol. The most polar fraction thus obtained was then separated further using high pressure liquid chromatography. This enabled the most polar components of diesel fuel to be separated fully [19].

### 5.2. Lubricity of separated fractions

Two fuels (Table 2, fuels 11 and 12) were subjected to displacement-percolation chromatography to yield nine fractions. These were then used in the high frequency reciprocating rig to measure their wear properties. Figure 7 shows the results, where the fractions of fuel 11 are labelled A-H in order of increasing polarity and those of fuel 12 are labelled 1-9. Figure 7 illustrates that the bulk of the wear resistance is concentrated in the most polar fractions of the fuels. Figure 8 shows the same results presented in terms of dynamic viscosity of the separate fractions at room temperature. All the fractions of fuel 11 were more viscous than any of those of fuel 12, but this seems to have negligible effect on wear compared with the effect of polarity. The efficacy of the most polar fractions in reducing wear can be seen in Fig. 9 where they are added to non-polar high wear fractions of the

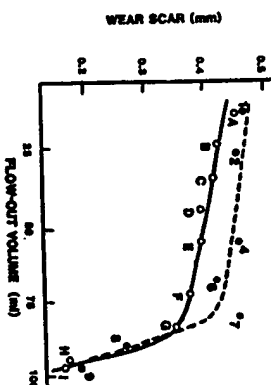


Fig. 7. Wear performance vs. flow-out volume from displacement chromatography: O, fuel 11; ●, fuel 12.



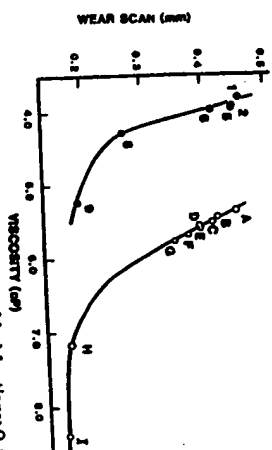


Fig. 8. Wear performance vs. viscosity of fuel fractions: O, fuel 11; □, fuel 12.

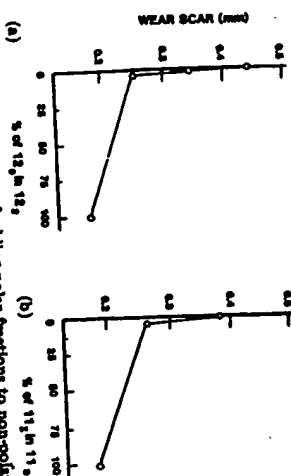


Fig. 9. Effect on wear of adding polar fractions to non-polar fractions: (a) fuel 12 (wear scar of whole fuel 12, 0.18 mm); (b) fuel 11 (wear scar of whole fuel 11, 0.21 mm).

corresponding fuel. Small percentages of the polar fraction were found to reduce wear very markedly.

Some researchers have suggested that aromatic components are important in reducing wear using diesel fuel, whereas others have favoured nitrogen, sulphur or acid component. In an attempt to assess the relative importance of aromatics, the aromatic content of each of the diesel fractions was determined and compared with wear performance.

Two techniques were employed. In one, absorption IR spectroscopy was used to provide the absorption ratio  $I_{1605}/I_{1464}$  at two wavelengths. This yields the overall aromatic content since  $1605 \text{ cm}^{-1}$  corresponds to the aromatic skeletal in-plane ring vibration whereas  $1464 \text{ cm}^{-1}$  represents the overall  $-\text{CH}_2-$  scissoring vibration. Figure 10 shows the results for fuel 11, and it can be seen that the aromatics are concentrated in the most polar fraction. (It should be noted that the fractions A, B etc. in this figure are similar to those in Figs. 7 and 8 but were produced in different chromatography runs.)

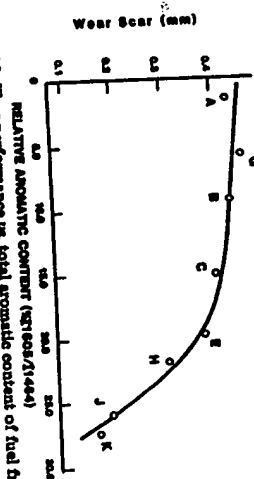


Fig. 10. Wear performance vs. total aromatic content of fuel fractions.

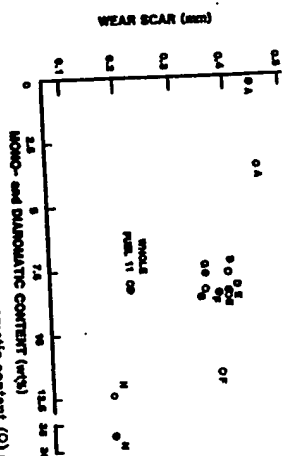


Fig. 11. Wear performance vs. mononuclear aromatic content (c) and diaromatic content (e) of fuel fractions.

A further analysis was carried out to measure separately the concentrations of mononuclear, diaromatics and polyaromatics in the diesel fuel fractions. This employed a UV absorption technique at three wavelengths as described by Balint [20]. Figures 11 and 12 show the results for fuel 11. The mononuclear and diaromatic contents do not seem to correlate well with wear. The most polar fraction, H, gave low wear but this trend was not clear from the less polar fractions, as will be discussed later. However, the high polyaromatic and polar content, as will be discussed later. However, the polyaromatic content does show a constant trend, with increasing polyaromatic concentration above 0.2 wt.-%, seeming to produce a slow reduction in wear, but much of the polyaromatic material was clearly very polar as well as being aromatic, as can be seen by its concentration in the final fraction.

Unfortunately this method of crude separation, by polarity, into fractions has some of the same deficiencies as the parametric studies on complete diesel fuels described earlier. Figure 12 shows that most of the

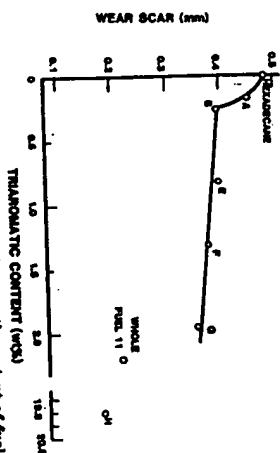


Fig. 12. Wear performance vs. polyaromatic content of fuel fractions.

polyaromatics stay with the other polar material in the most polar fraction and so the contributions of different polar materials cannot be distinguished.

To examine the lubricity of the various polar impurities individually would require a very lengthy separation procedure along the lines of that outlined earlier, using high pressure liquid chromatography. Instead, in this study, as in previous work [21], pure model impurities known from published work to be present in diesel fuels were added to fuels to study their effects on wear.

#### 6. Lubricity of model fuel additives

Four different classes of impurity were added to base fuels to test lubricity: aromatic, nitrogen compounds, sulphur compounds and oxygen compounds. The "base fuel" used was generally the high wear, severely hydrocracked fuel 13 (Table 1), although to study aromatics the pure paraffinic material, hexadecane, was also employed.

##### 6.1. Aromatic compounds

Figure 13 shows the effect of different concentrations of monoaromatic, diaromatic and tetraaromatic hydrocarbons in hexadecane. It can be seen that the monoaromatics and diaromatics have little effect on wear but that the tetraaromatic anthracene derivative produces a marked wear reduction for a concentration above 1 wt.%. The tetraaromatic hydrocarbon, pyrene, gave reduced wear at even lower concentrations.

##### 6.2. Sulphur compounds

A range of sulphur compounds were tested in fuel 13. The results are shown in Table 3 and indicate that all sulphur compounds tested are pro-wear to some extent and generally give higher wear at higher concentrations.

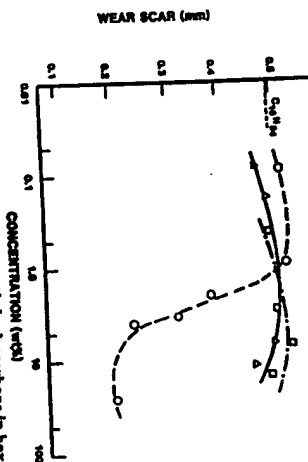


Fig. 13. Wear performance of aromatic hydrocarbons in hexadecane (base stock,  $C_{16}H_{34}$ ):  $\Delta$ , naphthalene;  $\circ$ , decylbenzene;  $\bullet$ , 9-methylanthracene.

TABLE 3

Wear test results using sulphur-containing model compounds

Test fuel	S from added compound (wt. %)	Wear scar diameter (mm)
Fuel 13	0	0.36
Fuel 13 + cyclopentyl sulphide	0.01 (100 ppm)	0.38
Fuel 13 + butyl isocyanide	0.01	0.40
Fuel 13 + dibenzyl disulphide	0.01	0.36
Fuel 13 + dibenzyl disulphide	1	0.49
Fuel 13 + n-dodecylsulphide	1	0.39

##### 6.3. Nitrogen compounds

Nitrogen compounds in fuel oils can be divided into two groups: basic, such as pyridines and quinolines, and non-basic, including pyrroles, carbazoles and indoles. Table 4 shows the wear results for both types of compound. All the nitrogen compounds reduced wear when dissolved in fuel 13 except for carbazole which could not be dissolved to concentrations above 100 ppm.

##### 6.4. Oxygen compounds

Table 5 shows the wear results from solutions of oxygen compounds. 8-hydroxyquinoline and medium- to long-chain carboxylic acids gave good reductions in wear even at concentrations as low as 10 ppm.

TABLE 4  
Wear test results using nitrogen-containing model compounds

Test fluid	N from added compound (wt.%)	Wear scar diameter (mm)
Fuel 13	0	0.35
Fuel 13 + pyridine	0.01	0.30
Fuel 13 + pyridine	1	0.19
Fuel 13 + pyroole	0.01	0.31
Fuel 13 + pyroole	1	0.16
Fuel 13 + quinoline	0.01	0.32
Fuel 13 + quinoline	1	0.19
Fuel 13 + indole	0.01	0.35
Fuel 13 + indole	1	0.22
Fuel 13 + carbazole	0.01	0.34
Fuel 13 + carbazole		

TABLE 5  
Wear test results using oxygen-containing model compounds

Test fluid	O from added compound (ppm)	Wear scar diameter (mm)
Fuel 13	0	0.35
Fuel 13 + 8-hydroxyquinoline	10	0.32
Fuel 13 + 8-hydroxyquinoline	100	0.18
Fuel 13 + 1,4-hydroquinone	100	0.32
Fuel 13 + hexanoic acid	100	0.23
Fuel 13 + hexadecanoic acid	1	0.33
Fuel 13 + hexadecanoic acid	10	0.32
Fuel 13 + hexadecanoic acid	100	0.18
Fuel 13 + hexadecanoic acid	300	0.17

### 6.5. Multicomponent mixtures

The effect of aromatic content on other polar impurities was studied by using multicomponent mixtures. Figure 14 compares the behaviour of 8-hydroxyquinoline in three fluids: (i) hexadecane, (ii) hydro-treated fuel 13 and (iii) hexadecane plus 2 wt.% 9-methylanthracene, a "model" diesel base fuel. It can be seen that the effect of the anthracene derivative and, by implication, of the polyaromatics in fuel 13 is to raise the threshold effective concentration of the hydroxyquinoline from 1 to 10 ppm, although the triaromatic's contribution to wear reduction is not affected. Figure 15 shows the behaviour of other polar additives in a hexadecane plus 2 wt.% 9-methyl-

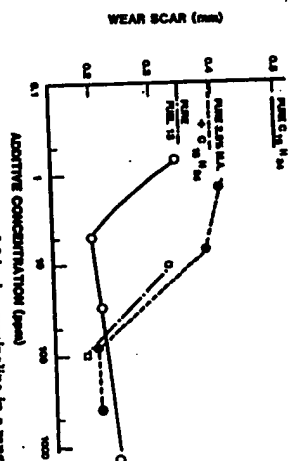


Fig. 14. Wear performance of 8-hydroxyquinoline in a range of base fuels: —○—,  $C_{16}H_{34}$ ; —○—, 2.5 wt.% 9-methylanthracene; —○—, fuel 13.

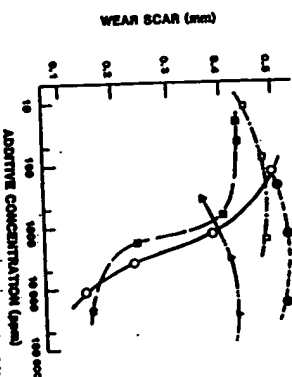


Fig. 15. Wear performance of a range of additives in a model base fuel: —○—, di-benzyl disulphide; —○—, benzyl mercaptan; —○—, pyroole; —○—, pyridine; —○—, thiophene.

anthracene mixture and illustrates the contrasting performance of nitrogen and sulphur additives.

### 7. Discussion

#### 7.1. Lubricity of diesel fuels

This study has shown that there is a considerable variation in the lubricity of automotive diesel fuels, as measured in wear tests. Separation of the fuels into fractions shows that this lubricity is not related to physical properties such as viscosity but to minor amounts of polar materials, which differ from fuel to fuel.

Both separation studies and tests with model additives have demonstrated that monoaromatic and diaromatic hydrocarbons make little contribution to wear control but that triaromatics and higher aromatics do reduce wear significantly at quite low concentrations. A large reduction in wear was observed for triaromatic concentrations of 2.0 wt.% or more. It is interesting to note that diesel fuels often have about this percentage of polyaromatics.

Sulphur constituents were consistently found to increase wear at the concentration found in diesel fuel. Nitrogen compounds consistently reduced wear but this reduction generally only became significant in the reduced wear range 0.1-1 wt.%, rather higher than that found in most concentration range 0.1-1 wt.%, rather higher than that found in most diesel fuel.

The most significant wear reduction was produced by oxygen-containing compounds with phenolic-type or carboxylic acid groups. Wear reduction occurred at a concentration of just a few parts per million, well within the range found in diesel fuel. A comparison of 8-hydroxyquinoline with that of quinoline indicates that the phenolic group plays a crucial role in the wear reduction process. It is interesting to note that 1,4-hydroquinone, which was found in this study to reduce wear, has been used as a dye in commercial diesel and gas oils intended for use in stationary machines and heating systems [22]. Dyeing is essential in these fuels which are duty rebated.

It thus appears that polyaromatics and oxygen constituents are likely to be the most important natural contributors to diesel fuel lubricity. Since the concentration at which polyaromatic hydrocarbons become effective in reducing wear corresponds to that found in fuel, the source of fuel and its treatments may well be of some significance. Oxygen analysis is rarely carried out on diesel fuel, partly because it is quite difficult to do and partly because of the problem of differentiating between compounded and dissolved oxygen. It appears from this study, however, that oxygen analysis after purging may well be a useful chemical indicator of fuel lubricity.

## 7.2. Thick film formation

In this paper so far the lubricity of diesel fuel and its components has not been illustrated but the mechanism by which this lubricity arises has been considered at all. The classical mechanism of action of lubricity agents involves adsorption of polar materials on rubbed metal surfaces to form a thin (often monomolecular) protective film [23, 24].

In recent work, however, Orton [25, 26] has suggested that diesel fuels can form thick reacted films on rubbed surfaces during prolonged sliding.

Orton based this conclusion on the following:

- (a) The electrical contact resistance between sliding surfaces increases steadily during extended running with diesel fuel, whilst friction correspondingly falls.
- (b) On halting running after an extended running period, considerable residual contact resistance remains between the static surfaces.

- (c) Scratching the exposed rubbed tracks with a Permapointer produces a step-like groove visible in the otherwise transparent and non-reflecting surface film.
- (d) When the surface, after rubbing in diesel fuel, is placed in a scanning electron microscope, a grease-like colloidal structure is observed.

An attempt was made to repeat Orton's work in the current study and all the effects listed above were noted. However, other observations complicated the situation. It was found that grooving of the surface film could be produced by scratching fuel-wetted metal surfaces even when these had not been rubbed. As in Orton's study, exposure of rubbed surfaces to scanning electron microscopy produced a grease-like structure. However, when the experiment was repeated but the rubbed surfaces exposed to a moderate vacuum ( $10^{-3}$  Torr) at 70 °C for some hours, no such grease-like structure was subsequently found in the scanning electron microscope. The structured layer rather than a reacted film may thus result from residual high boiling diesel components. It was also noted that the contact resistance increased steadily with time even in dry tests carried out in the absence of fuel, suggesting that the formation of oxide might play a part in electrical resistance phenomena.

Thus the mechanism of wear reduction by diesel fuels is by no means fully resolved. There are suggestions in the literature as to how such films might form, and these tie in well with the active components found in this study. Goldblatt [27] has suggested that polyaromatics can form stable radical anions and thence surface resins, whereas monoaromatics and diaromatics cannot. Nitrogen aromatics are also known to be able to oxidize quite easily [28] and thence to form chelating or bridging ligands which, in the presence of metal ions, might form high molecular weight material.

The correlation between electrical contact resistance and low wear, often cited as evidence for thick films, was most marked in the tests carried out in this study. Figure 16 shows typical resistance traces taken during four tests, all based on the hydro-treated fuel 13. Pure fuel gave a slight somewhat erratic increase in contact resistance. The addition of a pro-wear sulphur

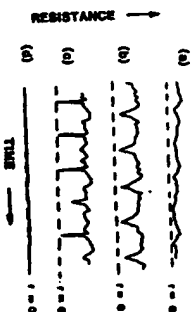


Fig. 16. Electrical contact resistance of four fuel mixtures: (a) fuel 13, wear scar of 1.36 mm; (b) fuel 13 + 1% pyridine, wear scar of 0.73 mm; (c) fuel 13 + 100 ppm 8-hydroxyquinoline, wear scar of 0.71 mm; (d) fuel 13 + 1 wt.% dibenzyl disulphide, wear scar of 1.94 mm.

additive removed any trace of contact resistance. Pyridine gave an electrical contact resistance and the very effective antiwear additive, 8-hydroxyquinoline, produced a particularly high contact resistance. The periodicity observed for the pyridine and 8-hydroxyquinoline solutions results from the collapse of the contact resistance at the end of each stroke, indicating that no insulating film can survive stroke reversal.

The concept of growth of thick films which prevent wear is attractive but, in the present authors' view, there is not yet sufficient evidence to be sure that such films form with fuel.

## 8. Conclusions

Diesel fuel lubricity, as measured by wear in the high frequency reciprocating machine, is to a large extent determined by polyaromatics and oxygen-containing polar impurities. Polyaromatics are effective at concentrations of a few weight per cent, whereas some oxygen compounds such as hydroxyquinolines and carboxylic acids reduce wear at concentrations of a few parts per million. Monosaromatic and diaromatic hydrocarbons have little influence on wear and most sulphur impurities are pro-wear.

## Acknowledgments

The authors would like to thank the British Council for their kind support for Mr. Dampier Wel which made the research possible. They are grateful too to Dr. John Sanger of Ricardo Engineering Consultants for all his help and advice.

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